Catalyst Additives to Enhance Mercury Oxidation and Capture

Quarterly Report

Period of Performance:

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Abstract

Preliminary research has shown that SCR catalysts employed for nitrogen-oxide reduction can effectively oxidize mercury. This report discusses initial results from fundamental investigations into the behavior of mercury species in the presence of SCR catalysts at Southern Research Institute. The testing was performed at Southern Research's Catalyst Test Facility, a bench-scale reactor capable of simulating gas-phase reactions occurring in coal-fired utility pollution-control equipment. Three different SCR catalysts are currently being studied in this project – honeycomb-type, plate-type, and a hybrid-type catalyst. The catalysts were manufactured and supplied by Cormetech Inc., Hitachi America Ltd., and Haldor-Topsoe Inc., respectively. Parametric testing was performed to investigate the contribution of flue-gas chemistry on mercury oxidation via SCR catalysts. Methods and procedures for experimental testing continue to be developed to produce the highest quality mercury-oxidation data. During this past quarter, it was discovered that long periods (12 - 24 hours) are required to equilibrate the catalysts in the system. In addition, after the system has been equilibrated, operational changes to temperature, gas concentration, or flow rate shifts the equilibrium, and steady-state must be reestablished, which can require as much as twelve additional hours per condition change.

In the last quarter of testing, it was shown that the inclusion of ammonia had a strong effect on the oxidation of mercury by SCR catalysts, both in the short-term (a transitional period of elemental and oxidized mercury off gassing) and the long-term (less steady-state mercury oxidation). All experiments so far have focused on testing the catalysts in a simulated Powder River Basin (PRB) flue-gas environment, which contains lower sulfur and chlorine than produced by other coals. In the next quarter, parametric testing will be expanded to include flue gases simulating power plants burning Midwestern and Eastern coals, which are higher in sulfur and chlorine. Also, the isolation of such gases as hydrogen chloride (HCl), ammonia (NH_3), and sulfur trioxide (SO_3) will be investigated. All of these efforts will be used to examine the kinetics of mercury oxidation across the SCR catalysts with respect to flue gas composition, temperature, and flow rate.

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Introduction

The objective of this project is to investigate the enhancement of elemental-mercury oxidation in coal-fired flue gas through catalysis. In addition to testing various catalyst materials, fundamental mechanisms associated with enhanced Hg-oxidation on SCR catalysts are being investigated. Data obtained in this work will be provided to Niksa Energy Associates (NES) and Reaction Engineering International (REI) to develop and improve models to predict mercury speciation in full-scale boilers, burning different coal types, ranging from sub-bituminous to high-volatile bituminous coals. Where necessary, Southern Research will develop semi-empirical mechanistic model(s) or correlations describing the mechanisms associated with catalysis-enhanced mercury oxidation. Results from the project will contribute to a greater understanding of mercury oxidation in flue gas.

Executive Summary

This Quarter, Southern Research Institute continues bench-scale reactor studies to evaluate the behavior of vapor-phase mercury in the presence of Selective Catalytic Reduction (SCR) catalysts. SCR catalysts are employed in coal-fired power plants for the reduction of nitrogen oxide (NO_x) emissions, but SCR catalysts also affect the speciation of other gases, such as mercury. Mercury primarily exists in two-different forms in coal-derived flue gas, $HgCl_2$ and the elemental form, and each type behaves somewhat differently in the "back-end" pollution control equipment of power plants. Oxidized mercury is readily captured in some of the commonly employed pollution control devices, such as wet scrubbers, while elemental mercury can be more difficult to capture. Therefore, a low-cost method of oxidizing mercury upstream of the wet scrubber is desired for coal-fired power plants that possess a wet scrubber. One of the best options would be a multi-pollutant solution, such as SCR catalysts for NO_x reduction and mercury oxidation, followed by a wet scrubber for mercury and sulfur capture downstream.

The Catalyst Test Facility (CTF) continues to be used to derive fundamental kinetic information about each catalyst investigated for mercury oxidation and capture. The CTF is described and illustrated in this quarterly report. At the core of the CTF is an extensive flue-gas simulation, gas flow, and metering system. Catalyst samples are supported in a 1-½" square (for honeycomb-type and hybrid catalysts) or 1-¼" x 2" rectangular (for plate-type) Pyrex reactor, through which the entire gas flow must pass. The CTF simulates clean (no particles) flue gas with all the major flue-gas species present, including CO, CO_2, H_2O, O_2, N_2, HCl, NO, SO_2, SO_3, and Hg°, in concentrations representative of that found in flue gases of existing power plants, burning specific coal types.

The simulated flue gas originates from compressed-gas cylinders. The gases from the cylinders are then mixed to known concentrations by use of precision mass-flow controllers. The appropriate moisture content is generated through precise control of water evaporation. Mercury is added to the system with a PS Analytical 10.534 Mercury Calibration System, which consists of a reservoir containing an inert substrate impregnated with elemental mercury maintained at constant temperature. The mercury reservoir supplies a saturated stream of elemental mercury which is diluted before mixing with the other gases. The simulated flue-gas stream is well mixed and preheated before entering the

reaction chamber. A 3-inch diameter by 3-feet long tube furnace heats the reactor, which allows the simulated flue gas to pass through the furnace while holding the catalyst samples in place.

Bench-scale SCR catalyst tests were conducted to elucidate the relationship between the SCR catalysts and mercury speciation under particular flue-gas environments. The testing procedures were established in the last quarter of 2004 and continue to be used during the current experiments. These procedures were described in the January 2005 Quarterly Report. The procedures described in that report were adjusted, based on discoveries made in the first quarter of 2005, described in the April 2005 Quarterly Report, and the test procedures were adapted again in the last quarter (2^{nd} Quarter of 2005). It was found that ammonia in the simulated flue gas affected the oxidation of mercury for each catalyst type. Specifically, after initially introducing the ammonia, a large spike of mercury was offgased over a period of approximately twelve hours. The baseline concentrations of mercury were approximately 10 $\mu g/Nm^3$, and ammonia injection increased this concentration to approximately 25 $\mu g/Nm^3$. After the initial spike, the total mercury concentration returned to the baseline concentration, but the oxidized portion was much less than before the ammonia was introduced (50% oxidation without ammonia, and <10% oxidation with ammonia). These discoveries were made while testing the honeycomb catalysts under simulated PRB flue-gas conditions. Because of the effects observed in these latest experiments, all future experiments will be conducted using ammonia in the simulated flue gas, although there are plans to isolate the effects of ammonia partial pressures on mercury oxidation, which shall begin near the end of the next quarter.

Next quarter, experiments will continue to progress through the test matrix described in this report. The kinetic rate of mercury oxidation by each catalyst will be examined. Also, the impact of varied partial pressures of ammonia, hydrogen chloride, and sulfur trioxide will be investigated. Fundamental rates and mechanisms of mercury oxidation on SCR catalysts will be elucidated from the results of these experiments.

Experimental

Figures 1-3 show pictures of the CTF's quartz furnace (micro-reactor), gas-conditioning bubblers for mercury speciation and stabilization prior to mercury monitoring, flue-gas continuous emission monitors (CEMs), and gas-flow control systems. Both elemental and total mercury are measured at the outlet of the CTF.

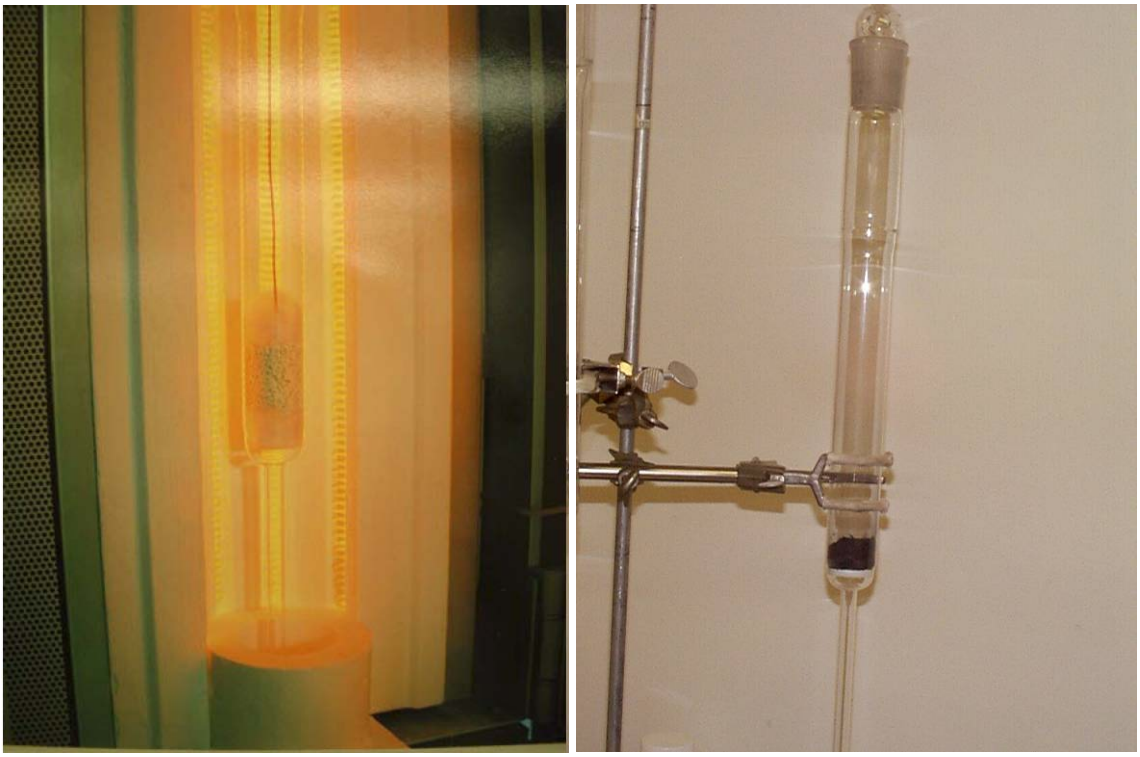

Figure 1. CTF quartz furnace at ~1000 °C (left) and outside of furnace (right).

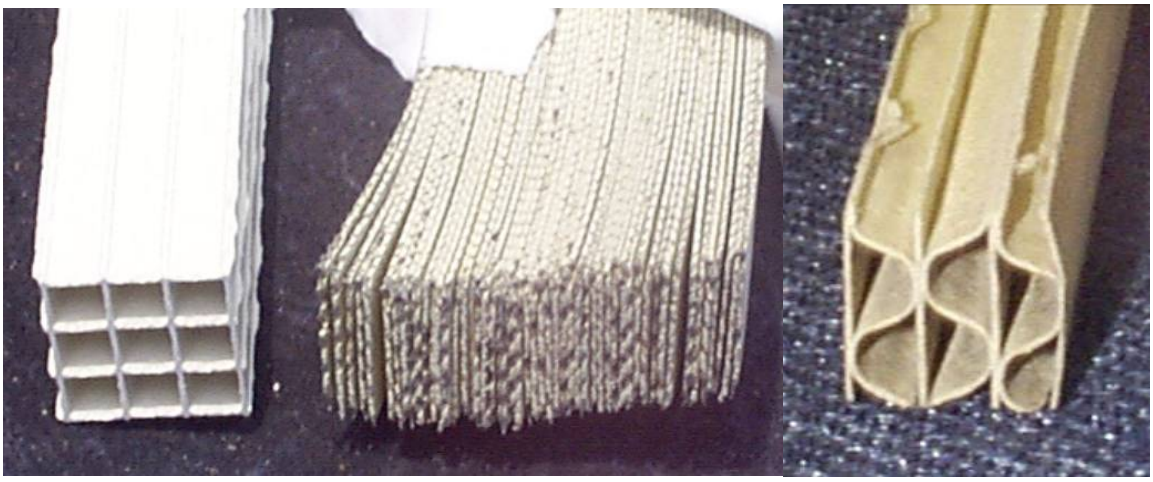

Figure 2. From left to right, honeycomb, plate, and hybrid SCR catalysts.

The CTF simulates clean (no particles) flue gas with all the major flue-gas species present, including CO, CO_2, H_2O, O_2, N_2, HCl, NO_x, SO_2, SO_3, and Hg°, in concentrations that exist in the flue gases of existing power plants, burning specific coal types. The simulated flue gas is originated from compressed-gas cylinders. The gases from the cylinders are then mixed to known concentrations by use of mass flow controllers. The appropriate moisture content is generated through precise control of water evaporation. Mercury is added to the system with a PS Analytical 10.534 Mercury Calibration System,

which consists of a reservoir containing an inert substrate impregnated with elemental mercury maintained at constant temperature. The mercury reservoir supplies a saturated stream of elemental mercury which is diluted before mixing with the other gases. The simulated flue-gas stream is well mixed and preheated before entering the reaction chamber. A 3-inch diameter by 3-foot long tube furnace heats the reactor, which allows the simulated flue gas to pass through the furnace while holding the catalyst samples in place. The three different catalyst samples are shown in Figure 2.

The majority (i.e., over 95%) of NO_x in the flue gas of coal-fired boiler systems is in the form of NO. Hence, NO is generally used in this work to simulate the NO_x in the flue gas, except for experiments specifically conducted to observe the effect of NO_2. In such cases, mixed NO/NO_2 gas bottles will be used to simulate the NO_x in the flue gas. With only NO in the flue gas, the NO_x reduction reaction is simplified to the following:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

All heated sections of the micro-reactor within the CTF system are made of quartz glass to limit side reactions that might occur as a result of wall effects. A semi-continuous emission monitor (SCEM) is employed to detect the mercury levels exiting the reaction chamber. A gas-conditioning system is used to convert all Hg into the elemental form, for detection using a combined gold-trap and atomic fluorescence monitor. A Tekran Model 2573A Mercury Vapor Analyzer is used to detect the elemental mercury. Along with mercury, simultaneous measurements of oxygen, carbon dioxide, nitrogen oxides, and sulfur dioxide are made using continuous emission monitors. Figure 4 shows a schematic of the CTF system layout.

Figure 3. Catalyst Test Facility (CTF)**.**

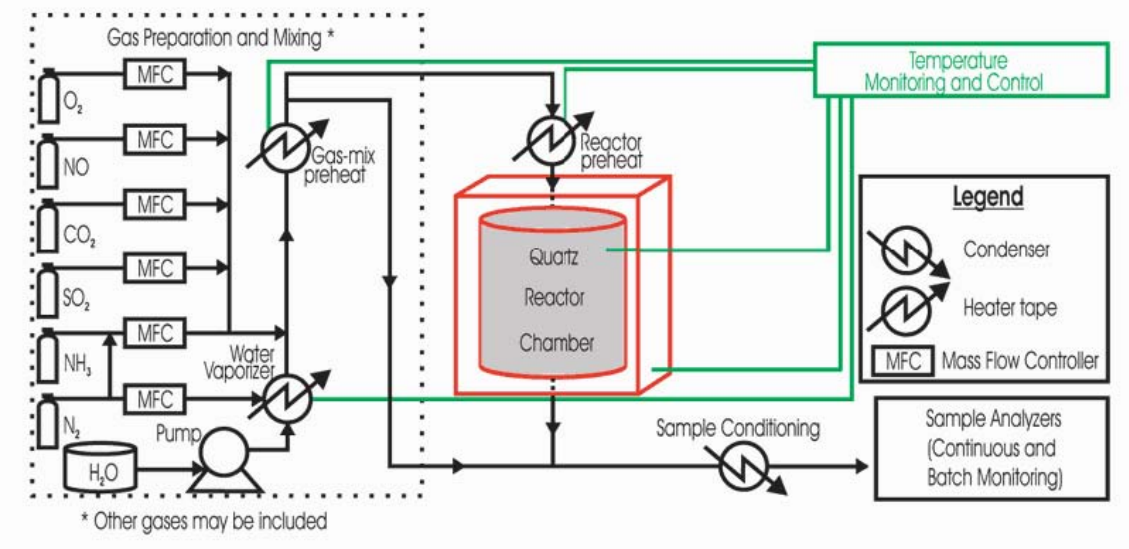

Figure 4. CTF gas-flow system.

For details concerning the validation and operation of the CTF, refer to the March 04 DOE Quarterly Report for the Calcium-Based Hg-Sorbents project conducted at Southern Research Institute [1] and a previous Quarterly Report on this project [2].

Results and Discussion

Mercury Oxidation Testing

The oxidation of mercury via SCR catalysts is an important step in the mercury-removal process. In the previous quarter (January 1st – March 30th, 2005), experiments were performed to build an understanding of the mechanisms governing mercury oxidation by three catalyst types and three characteristic flue gas types: 1) PRB, high-Sulfur, 2) high-chloride bituminous, and 3) mid-sulfur, mid-chloride bituminous. These experiments were continued in the current quarter (April 1st – June 30th, 2005). All experiments thus far have been conducted while simulating a PRB coal-derived flue-gas environment. Three temperature conditions were tested, 650, 700, and 750 ^{o}F, which are characteristic of the minimum, average, and maximum operating temperatures of many SCR reactors employed for the coal-fired utility industry. The test matrix currently being pursued this year is defined in Tables 1 and 2.

Initial testing showed that SCR catalysts can oxidize mercury in simulated coal-fired flue-gas conditions, but the extent of mercury oxidation was shown to be highly dependent upon the flue-gas temperature and the concentration of gas species, particularly HCl, NH_3, and SO_2. In addition, initial testing showed that when the equilibrium concentrations of mercury were affected by changes in gas concentrations or temperature, a long period (>12 hours) was required for the concentrations to stabilize.

Table 1. Test Parameters and Notations for Table 2.

Catalyst Type	Temperature (^{o}F)
1. Plate 2. Honey Comb 3. Hybrid	1. 600 2. 675 3. 750
Simulated Flue Gas Type (SFGT)	**Measurements**
1. PRB Coal 2. Low-sulfur & chlorine bituminous 3. High-sulfur & chlorine bituminous 4. Isolation of HCl, NH_3, and SO_3	1. SO_2/SO_3 Conversion 2. NO/NO_2 outlet concentrations 3. Mercury Removal 4. Mercury Oxidation 5. Complete gas composition, flows, etc.

Table 2. Bench-scale Experimental Test Matrix.

Condition Number	Catalyst Type	Temp.	SFGT	Meas.
1	1	1	1, 4	1 – 5
2	1	2	1, 4	1 – 5
3	1	3	1, 4	1 – 5
4	1	1	2, 4	1 – 5
5	1	2	2, 4	1 – 5
6	1	3	2, 4	1 – 5
7	1	1	3, 4	1 – 5
8	1	2	3, 4	1 – 5
9	1	3	3, 4	1 – 5
10	2	1	1, 4	1 – 5
11	2	2	1, 4	1 – 5
12	2	3	1, 4	1 – 5
13	2	1	2, 4	1 – 5
14	2	2	2, 4	1 – 5
15	2	3	2, 4	1 – 5
16	2	1	3, 4	1 – 5
17	2	2	3, 4	1 – 5
18	2	3	3, 4	1 – 5
19	3	1	1, 4	1 – 5
20	3	2	1, 4	1 – 5
21	3	3	1, 4	1 – 5
22	3	1	2, 4	1 – 5

Effects of Ammonia on Mercury Oxidation

In this last quarter, the effects of ammonia were investigated. Prior to the current quarter, all experiments had been conducted without including ammonia in the simulated flue gas. Ammonia was fed as dilute gas mixed with nitrogen, and the ammonia mixture was preheated before joining the reactor flow-system prior to the catalyst chamber. Ammonia was introduced to the reactor flow system through a 3-way valve. When ammonia was not required, the valve was positioned to feed pure nitrogen. This allowed the volumetric concentration of simulated flue-gas species to be maintained, when the valve was switched to introduce ammonia. Including ammonia in the simulated flue gas had a strong effect on the oxidation of mercury by SCR catalysts.

The experimental procedure for the experiments (including ammonia), began by collecting baseline mercury-concentration measurements. This was performed using a blank reactor that did not contain catalyst, which allowed the baseline oxidation rates to be determined when there was no catalyst present. During the baseline measurements, ammonia was not included in the simulated flue gas, because of the potential for reaction of ammonia with sulfur oxides. Ammonium bisulfate (NH_4HSO_4) will form at elevated concentrations of ammonia in the presence of sulfur-oxide gases. Ammonium bisulfate will precipitate at lower gas temperatures, and in past experiments, this precipitation has caused the reactor-flow system to plug. When the catalyst is installed in the flow system, the ammonia is consumed by reaction with nitrogen oxides (See Equation 1), and the formation of ammonium bisulfate will not occur. Therefore, when the blank reactor was installed, the ammonia was turned off, and when the reactor loaded with catalyst was installed, the ammonia was turned on. Nevertheless, enough data has been taken with SCR catalysts without ammonia injection and sorbent tests with both SO_2 and NO_x present to assure that excluding NH_3 from the baseline tests does not significantly alter the mercury-oxidation baseline.

At the conclusion of the baseline measurements, the blank reactor was removed from the furnace, and a reactor loaded with catalyst was inserted in its place. In the initial experiments, the ammonia was not immediately turned on, but first the catalyst was allowed to reach steady state in the same simulated flue-gas environment as that from the blank reactor experiments. During this time the concentrations of elemental and oxidized mercury fell initially, and over a period of approximately twelve hours the concentration of total mercury approached that witnessed under baseline conditions (~10 $\mu g/Nm^3$), but the proportion of oxidized mercury was approximately 60% (at 700^{o}F catalyst temperature), where baseline conditions produced only 10% oxidized mercury. This represents a fifty percent gain in mercury oxidation without ammonia in the simulated flue gas.

After steady-state mercury concentrations were recorded without ammonia, it was then included in the simulated flue gas. This resulted in an initial spike in elemental and oxidized mercury concentrations, followed by a slow reduction back to the baseline concentrations. At steady-state mercury concentration, the total mercury was approximately equal to the baseline concentration (~10 $\mu g/Nm^3$), but the oxidized portion had been reduced to near zero percent at 650 and 750^{o}F catalyst temperatures and to baseline oxidation at 700 ^{o}F. The addition of ammonia appeared not only to inhibit the ability of the catalyst to oxidize mercury, but it also reduced a portion of the oxidized mercury that was oxidized under baseline conditions.

Effects of Temperature on Mercury Oxidation

The effect of temperature on mercury oxidation by SCR catalysts was investigated in the current quarter. The findings from the current experiments were that an increase in temperature caused a temporary spike in total-mercury concentration, but given time to return to steady state, the total mercury concentration was unaffected. The oxidation rates were also unaffected, and remained near zero percent, at catalyst temperatures**Error! Bookmark not defined.** of 650, 700 and 750°F. It is expected that the other two remaining flue-gas types to be tested under this research program will increase the amount of mercury oxidation (even in the presence of ammonia). The effect of temperature on mercury oxidation will also be investigated for these SCR catalysts.

The conditions from the above mentioned experiments are listed in Table 1. The gas concentrations in Table 1 represent a simulation of a plant burning PRB coal. The flow rate was adjusted (from 5 to 7.5 lpm) during the current quarter to prevent flow problems in the mercury sampling system and to sustain a large enough flow that all gas measurements could be made simultaneously.

Table 3. Test conditions for SCR catalyst, mercury oxidation experiments.

Parameter	**Value**	**Units**
Temperature	650, 700, and 750	oF
Flow rate	7.5	slpm (@ 70oF and 1 atm)
Gas Concentrations[1]	Simulated Powder River Basin Flue Gas	
Oxygen	5	% (dry, by volume)
Carbon Dioxide	15	% (dry, by volume)
Nitric Oxide	300	ppm (dry, by volume)
Ammonia	0/300	ppm (dry, by volume)
Sulfur Dioxide	500	ppm (dry, by volume)
Hydrogen Chloride	2	ppm (dry, by volume)
Mercury	10	μg/Nm^3 (dry)
Nitrogen	Balance	% (dry, by volume)

Conclusions

Initial tests have demonstrated the ability of SCR catalysts to promote mercury oxidation in coal-derived flue-gas environments, but this oxidation has shown to be inhibited by ammonia. Also, the experimental procedure has shown to require overnight operation to achieve the >12 hours of testing required to reach steady state, following changes in temperature and gas composition. There was no effect of temperature on mercury oxidation at 650, 700, and 750 °F, for the simulated flue-gas conditions tested in the current quarter. However, due to low mercury oxidation for all temperature conditions with the simulated PRB flue gas, it is probable that an effect of temperature may be observed for the other (higher HCl concentration) flue-gas types to be tested next quarter.

[1] Gas concentrations are listed at the actual oxygen concentration of 5% by volume.

Future Work

Testing of mercury oxidation across SCR catalysts will continue during the next quarter. The effects of different mercury and ammonia concentrations will be investigated, and the data will be used to elucidate the mechanisms governing the oxidation of mercury by SCR catalysts. Further, experiments will be conducted using different flue gases for specific coal types, varied levels of individual gas components (HCl, Hg, SO_3, and NH_3), and multiple gas temperatures. The data generated from these experiments will be used to develop a clear understanding of mercury oxidation across SCR catalysts, relative to full-scale coal-fired power plants.

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